

PATENT ABSTRACTS OF JAPAN

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(21)Application number : 05-091958

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LTD

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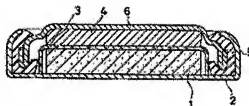
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UEMACHI YASUSHI
TONOMURA TADASHI

(54) REVERSIBLE ELECTRODE

(57)Abstract:

PURPOSE: To enable charging/discharging of large current even at a room temperature by including a polymer of organic disulfide compound which enables oxidation-reduction, a conductive material and a binding agent, and thereby enabling charging and discharging.

CONSTITUTION: A coin type battery for which an Li metal negative electrode 4 is used, comprises a positive electrode 1, a case 2, a separator 3, a gasket 5, and a sealing plate 6. The polymer forming the electrodes 1, 4 contains an organic disulfide compound serving as active material, a binding agent and a conductive material, and provides a reversible electrode. The polymer of the organic disulfide compound provides a reversible electrode which enables charging/discharging of large current even at a room temperature, and even when the electrode is used as the positive electrode 1 for a lithium electrode, discharging can be carried out without impairing high energy density. An excellent battery of stable cycle life is thus provided.



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CLAIMS

[Claim(s)]

[Claim 1]A reversibility electrode containing a polymer, a conducting material, and a binder of an organic disulfide system compound in which an oxidation-reduction reaction is possible.

[Claim 2]The reversibility electrode according to claim 1 whose polymer of said organic disulfide system compound is a homopolymer of 2,5-dimercapto-1,3,4-thiadiazole or thiocyanuric acid, or both copolymer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the reversibility electrode used for electrochemical elements, such as a rechargeable battery or an electrochromic element.

[0002]

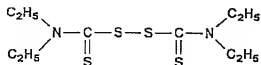
[Description of the Prior Art]If a conductive polymer is used for an electrode material, it is lightweight, and since realization of electrochemical elements, such as a biochemistry sensor using the cell of high energy density, the electrochromic element of a large area, and microelectrode, is expectable, practical use of the conductive polymer electrode is considered briskly. It started in the polyacetylene which Shirakawa and others discovered in 1971, pi electron conjugated system conductive polymers, such as poly aniline, polypyrrole, poly acene, and a polythiophene, were found out, and the rechargeable battery using these as an electrode has reached for developing. As an energy density of the electrode using these conductive polymers, it will be 250 - 400 Wh/kg per conductive polymer, and the effectual energy density in the stage which constitutes a actual cell will be these about 10 to 30%, i.e., 20 - 120 Wh/kg. On the other hand, the disulfide system compound is proposed by US,4,833,048,B as organic materials which can expect one 4 times [twice to] the high energy density of this. It is expressed with the easiest form R-S-S-R, an SS linkage cleaves by electrolytic reduction, and this compound generates the salt expressed with the cation (M^+) in an electrolytic bath, and R-S⁻-M⁺. This salt has the character to return to original R-S-S-R again by electrolytic oxidation. The metal-sulfur rechargeable battery which combined the metal M which supplies a cation (M^+) and is caught, and a disulfide system compound is proposed by the above-mentioned United States patent, and it is supposed that an even match or the energy density beyond it is expectable in 150 Wh/kg and the usual rechargeable battery per cell.

[0003]However, the disulfide system compound proposed, As the artificers of US,4,833,048,B have reported by the journal electrochemical society, the 136th volume, and 2570-2575 pages (1989), For example, in electrolysis of the tetraethylthiuram disulfide (** 1), the potential of oxidation and reduction is separated V or more [1].

According to the place which an electrode reaction theory teaches, the electrochemical reaction in such a material, The electronic transition process was very late, therefore it had SUBJECT that it was difficult to take out the big current corresponding to practical use, for example, the current more than 1 mA/cm², and it was restricted to the 100-200 ** use in an elevated temperature, near the room temperature.

[0004]

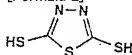
[Formula 1]



[0005]According to the place which the same artificers have reported by the journal electrochemical society, the 139th volume, and 2077-2081 pages (1992). The homopolymer of 2,5-dimercapto-1,3,4-thiadiazole (** 2) or ethanedithiol (** 3), or both copolymer, The cell which used the copolymer of 2,5-dimercapto-1,3,4-thiadiazole and 2-mercaptoethyl ether (** 4), etc. as the active material is evaluated. Although they constitute the cell combining these electrodes that mixed polyethylene oxide and a salt with a polymer and carbon as ion-conductive Polymer Division, the electrolyte which consists of polyethylene oxide and a salt, and Li metal, they need an operation at 90-110 **.

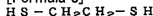
[0006]

[Formula 2]



[0007]

[Formula 3]



[0008]

[Formula 4]



[0009]According to the place which the same artificers have reported by the journal electrochemical society, the 137th volume, and 1191-1192 pages (1990). The cell using anode graphite and negative-electrode lithium has reported having repeated charge and discharge with the high current density of $16\text{mA}/\text{cm}^2$ at the room temperature by using as battery active material the tetraethylthiuram disulfide dissolved in dimethyl sulfoxide. Although $3.4\text{mA}/\text{cm}^2$ was examining the cycle characteristic, since depth of discharge was stopped to 10% in any case, it was low capacity.

[0010]

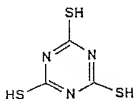
[Problem(s) to be Solved by the Invention]As mentioned above, near the room temperature, the electrode which uses as an active material the organic disulfide system compound by which the conventional proposal is made was difficult to take out a high current, and lacking in practicality — capacity is low. This invention solves such a problem and an object of this invention is to provide the reversibility electrode in which the charge and discharge in a high current are possible also at a room temperature.

[0011]

[Means for Solving the Problem]A reversibility electrode of this invention uses a polymer of an organic disulfide system compound as an active material, and contains a binder and a conducting material further. As a polymer of an organic disulfide system compound, a homopolymer of 2,5-dimercapto-1,3,4-thiadiazole or thiocyanuric acid (** 5) or both copolymer is used. In order to obtain an electrode for rechargeable batteries excellent in especially reversibility, it is preferred that a mole ratio of 2,5-dimercapto-1,3,4-thiadiazole and thiocyanuric acid uses a copolymer which is 1:1 to 20:1.

[0012]

[Formula 5]

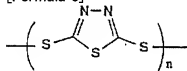


[0013]

[Function]The polymer of the 2,5-dimercapto-1,3,4-thiadiazole which constitutes the electrode of this invention is expressed with ** 6, and the thing of the degree of polymerization $n = 2-50$ and the molecular weights 300-7500 is used.

[0014]

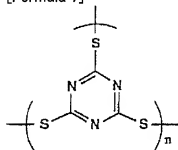
[Formula 6]



[0015]The polymer of thiocyanuric acid is expressed with ** 7, and the thing of the degree of polymerization $n = 2-50$ and the molecular weights 350-8500 is used.

[0016]

[Formula 7]



[0017]Polymers of an organic JISUFIRUDO system compound, such as these polymers and a copolymer of 2,5-dimercapto-1,3,4-thiadiazole and thiocyanuric acid, give the reversibility electrode in which high current charge and discharge are possible also at a room temperature. Without spoiling the feature of having the high energy density of a lithium cell, even if it uses as an anode for lithium cells, charge and discharge are possible and the cycle characteristic stable moreover is given. In order to obtain the anode for rechargeable batteries excellent in especially reversibility, it is preferred that the mole ratio of 2,5-dimercapto-1,3,4-thiadiazole and thiocyanuric acid uses the copolymer which is 1:1 to 20:1. A fluoro-resin, ion-conductive polymer, etc. are used as a binder. As ion-conductive polymer, the copolymer of end crosslinked polymer of the copolymer of polyethylene oxide, and ethylene oxide and propylene oxide, polyacrylonitrile, acrylonitrile, and methacrylic acid, etc. are raised. As a conducting material, conductive polymers which are carbon fiber, black lead, graphite, a metal powder, etc., such as others and poly aniline, a polythiophene, polypyrrole, and poly para-phenylene, can be used.

[0018]When using as an anode of a lithium secondary battery, the electrolysis solution which dissolved alkali metal salt in the nonaqueous solvent is used as an electrolyte effective in an operation at a room temperature. As a nonaqueous solvent, the mixed liquor of propylene carbonate, propylene carbonate, and dimethoxyethane, The mixed liquor of propylene carbonate and a tetrahydrofuran, the mixed liquor of sulfolane and dimethoxyethane, The mixed liquor of sulfolane and a tetrahydrofuran, etc. are raised for lithium perchlorate and lithium trifluoromethanesulfonate, tetrafluoride lithium borate, lithium hexafluorophosphate, etc. as alkali metal salt again, respectively.

The polymer electrolyte having contained these electrolysis solutions can also be used. As such polymer, there are end crosslinked polymer of polyethylene oxide or polypropylene oxide, and crosslinked polymer of the copolymer of ethylene oxide and propylene oxide, polyacrylonitrile, acrylonitrile, copolymerization polymer of methacrylic acid, etc. However, it is not limited to these. [0019]

[Example] Below, the example of this invention is described in detail.

[Working example 1] 10 g of 2,5-dimercapto-1,3,4-thiadiazole (made in Tokyo Chemicals) and 5.85 g of lithium hydroxide monohydrate were dissolved in 200 ml of water, and it was considered as A liquid. Independently, the iodine 16.9g and 33.9 g of lithium iodide dihydrate were dissolved in 400 ml of water, and it was considered as B liquid. Stirring A liquid, adding B liquid was continued and oxidative polymerization was performed. After having separated the generated precipitation, and hexane, acetone, and water having washed one by one and removing an unreacted material, vacuum drying was performed at 60 °C for 10 hours. Yield is 90% and output melted into neither water nor ethanol nor ether. Since it was meltable to these solvents in the monomer, it checked that output was a polymer. 5 g and 2 g of polytetrafluoroethylene (made by poly chlorofluorocarbon F-104 Daikin Industries) are mixed in the polymer powder 1g of the 2,5-dimercapto-1,3,4-thiadiazole created by the above-mentioned method, and the end (made by graphitization gaseous phase method carbon fiber Showa Denko) of carbon powder, The lump of gum paste state was created with the mortar. This lump was ground and it was considered as positive electrode mixture. Pressing of 150 mg of this mixture was carried out into the positive electrode case using the metallic mold. Tetrafluoride lithium borate was dissolved in the mixed solvent of the volume ratio 1:1 of propylene carbonate and dimethoxyethane by 1 M concentration, and it was considered as the electrolysis solution.

[0020] The coin type cell as shown in drawing 1 using an aforementioned anode, electrolysis solution, and Li metal negative electrode was constituted. As for a separator and 4, in drawing 1, an anode and 2 are [a gasket and 6] obturation boards a negative electrode and 5 a case and 3 1. When the cyclic test of charge and discharge was done for the above-mentioned cell between 3.5V and 2.65V by the constant current of 1 mA/cm², the discharge curve which has flat discharge potential was obtained, early capacity was as high as 90% of the theoretical value, and 80% of capacity of initial capacity was maintained by the 50th time. When charge and discharge were repeated between 3.5V and 2.0V, early capacity was as high as 90% of the theoretical value, and 50% of capacity of initial capacity was maintained by the 50th time.

[0021] [Working example 2] 10.0 g of thiocyanuric acid (made in Tokyo Chemicals) and 7.10 g of lithium hydroxide monohydrate were dissolved in 200 ml of water, and it was considered as A liquid. Independently, the iodine 21.5g and 43.2 g of lithium iodide dihydrate were dissolved in 400 ml of water, and it was considered as B liquid. Stirring A liquid, adding B liquid was continued and oxidative polymerization was performed. After having separated the generated precipitation, and hexane, acetone, and water having washed one by one and removing an unreacted material, vacuum drying was performed at 60 °C for 10 hours. Yield is 90% and output melted into neither water nor ethanol nor ether. Since it was meltable to these solvents in the monomer, it checked that output was a polymer.

[0022] 5 g and 2 g of polytetrafluoroethylene (made by poly chlorofluorocarbon F-104 Daikin Industries) were mixed in the homopolymer powder 1g of the thiocyanuric acid created by the above-mentioned method, and the end (made by graphitization gaseous phase method carbon fiber Showa Denko) of carbon powder, and the lump of gum paste state was created with the mortar. This lump was ground and it was considered as positive electrode mixture. Pressing of 150 mg of this mixture was carried out into the positive electrode case using the metallic mold, and the same coin type cell as working example 1 was constituted. When the cyclic test of charge and discharge was done for this cell between 3.5V and 2.55V by the constant current of 1 mA/cm², the discharge curve which has flat discharge potential was obtained, early capacity was as high as 70% of the

theoretical value, and 56% of capacity of initial capacity was maintained by the 50th time.

[0023][Working example 3] 7.5 g of 2,5-dimercapto-1,3,4-thiadiazole (made in Tokyo Chemicals), 2.5 g of thiocyanuric acid (made in Tokyo Chemicals), and 6.07 g of lithium hydroxide monohydrate were dissolved in 200 ml of water, and it was considered as A liquid. Independently, the iodine 18.4g and 36.9 g of lithium iodide dihydrate were dissolved in 400 ml of water, and it was considered as B liquid. Stirring A liquid, adding B liquid was continued and oxidative polymerization was performed. After having separated the generated precipitation, and hexane, acetone, and water having washed one by one and removing an unreacted material, vacuum drying was performed at 60 °C for 10 hours. Yield is 87% and output melted into neither water nor ethanol nor ether. Since it was meltable to these solvents in the monomer, it checked that output was a polymer. 5 g of 2,5-dimercapto-1,3,4-thiadiazole, the copolymer powder 1g of the mole ratio of 3:1 of thiocyanuric acid, and the end of carbon powder (made by graphitization gaseous phase method carbon fiber Showa Denko) and polytetrafluoroethylene (poly chlorofluorocarbon .) which were created by the above-mentioned method F-104 The Daikin Industries make 2g was mixed and the lump of gum paste state was created with the mortar. This lump was ground and it was considered as positive electrode mixture. Pressing of 150 mg of this mixture was carried out into the positive electrode case using the metallic mold, and the coin type cell was constituted like working example 1.

[0024]When the cyclic test of charge and discharge was done for this cell between 3.5V and 2.55V by the constant current of 1 mA/cm², the discharge curve which has flat discharge potential was obtained, early capacity was as high as 77% of the theoretical value, and 90% of capacity of initial capacity was maintained by the 50th time.

[Working example 4] 8.33 g of 2,5-dimercapto-1,3,4-thiadiazole (made in Tokyo Chemicals), 1.67 g of thiocyanuric acid (made in Tokyo Chemicals), and 6.00 g of lithium hydroxide monohydrate were dissolved in 200 ml of water, and it was considered as A liquid. Independently, the iodine 18.2g and 36.4 g of lithium iodide dihydrate were dissolved in 400 ml of water, and it was considered as B liquid. Stirring A liquid, adding B liquid was continued and oxidative polymerization was performed.

[0025]After having separated the generated precipitation, and hexane, acetone, and water having washed one by one and removing an unreacted material, vacuum drying was performed at 60 °C for 10 hours. Yield is 85% and output melted into neither water nor ethanol nor ether. Since it was meltable to these solvents in the monomer, it checked that output was a polymer. 5 g of 2,5-dimercapto-1,3,4-thiadiazole, the copolymer powder 1g of the mole ratio of 5:1 of thiocyanuric acid, and the end of carbon powder (made by graphitization gaseous phase method carbon fiber Showa Denko) and polytetrafluoroethylene (poly chlorofluorocarbon .) which were created by the above-mentioned method F-104 The Daikin Industries make 2g was mixed and the lump of gum paste state was created with the mortar. This lump was ground and it was considered as positive electrode mixture. Pressing of 150 mg of this mixture was carried out into the positive electrode case using the metallic mold, and the coin type cell was constituted like working example 1. When the cyclic test of charge and discharge was done between 3.5V and 2.55V by the constant current of 1 mA/cm², the discharge curve which has flat discharge potential was obtained, early capacity was as high as 87% of the theoretical value, and 98% of capacity of initial capacity was maintained by the 50th time.

[0026][Working example 5] 9.10 g of 2,5-dimercapto-1,3,4-thiadiazole (made in Tokyo Chemicals), 0.90 g of thiocyanuric acid (made in Tokyo Chemicals), and 5.72 g of lithium hydroxide monohydrate were dissolved in 200 ml of water, and it was considered as A liquid. Independently, the iodine 17.3g and 34.7 g of lithium iodide dihydrate were dissolved in 400 ml of water, and it was considered as B liquid. Stirring A liquid, adding B liquid was continued and oxidative polymerization was performed. After having separated the generated precipitation, and hexane, acetone, and water having washed one by one and removing an unreacted material, vacuum drying was performed at 60 °C for 10 hours. Yield is 80% and output melted into neither water nor ethanol nor ether. Since it was meltable

to these solvents in the monomer, it checked that output was a polymer. 5 g of 2,5-dimercapto-1,3,4-thiadiazole, the copolymer powder 1g of the mole ratio of 10:1 of thiocyanuric acid, and the end of carbon powder (made by graphitization gaseous phase method carbon fiber Showa Denko) and polytetrafluoroethylene (poly chlorofluorocarbon F-104.) which were created by the above-mentioned method The Daikin Industries make 2g was mixed and the lump of gum paste state was created with the mortar. This lump was ground and it was considered as positive electrode mixture. Pressing of 150 mg of this mixture was carried out into the positive electrode case using the metallic mold, and the coin type cell was constituted like working example 1. When the cyclic test of charge and discharge was done between 3.5V and 2.55V by the constant current of 1 mA/cm², the discharge curve which has flat discharge potential was obtained, early capacity was as high as 82% of the theoretical value, and 95% of capacity of initial capacity was maintained by the 50th time. [0027][Comparative example] 5 g and 2 g of polytetrafluoroethylene (made by poly chlorofluorocarbon F-104 Daikin Industries) are mixed in the 2,5-dimercapto-1,3,4-thiadiazole (made in Tokyo Chemicals) powder 1g, and the end (made by graphitization gaseous phase method carbon fiber Showa Denko) of carbon powder, The lump of gum paste state was created with the mortar. This lump was ground and it was considered as positive electrode mixture. Pressing of 150 mg of this mixture was carried out into the positive electrode case using the metallic mold, and the coin type cell was constituted like working example 1. When the cyclic test of charge and discharge was done between 3.5V and 2.55V by the constant current of 1mA/[cm]², in the first charge and discharge, the discharge curve which has flat discharge potential was obtained, but it became 10% of capacity of initial capacity by the 10th time. The above result was summarized in Table 1 and shown. While the charge and discharge in a high current are comparatively possible for the electrode by working example, its capacity factor is also high and the cycle life is also excellent, so that clearly from Table 1.

[0028]

[Table 1]

	正極利用率 (%)	
	2サイクル目	50サイクル目
実施例1	90	72
実施例2	70	40
実施例3	77	70
実施例4	87	85
実施例5	82	78
比較例1	80	8

[0029]In working example, although metal lithium is used as a negative electrode of a rechargeable battery, the carbon compound negative electrode etc. which comprise a lithium alloy, carbon and Al powder, and solid electrolytes, such as Li-aluminum, can be used.

[0030]

[Effect of the Invention]According to this invention, the reversibility electrode in which the charge and discharge in a high current are comparatively possible can be obtained.

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TECHNICAL FIELD

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PRIOR ART

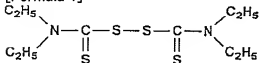
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[0004]

[Formula 1]

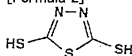


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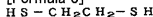
[0006]

[Formula 2]



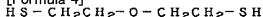
[0007]

[Formula 3]



[0008]

[Formula 4]



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EFFECT OF THE INVENTION

[Effect of the Invention]According to this invention, the reversibility electrode in which the charge and discharge in a high current are comparatively possible can be obtained.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention]As mentioned above, near the room temperature, the electrode which uses as an active material the organic disulfide system compound by which the conventional proposal is made was difficult to take out a high current, and lacking in practicality — capacity is low. This invention solves such a problem and an object of this invention is to provide the reversibility electrode in which the charge and discharge in a high current are possible also at a room temperature.

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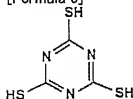
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MEANS

[Means for Solving the Problem]A reversibility electrode of this invention uses a polymer of an organic disulfide system compound as an active material, and contains a binder and a conducting material further. As a polymer of an organic disulfide system compound, a homopolymer of 2,5-dimercapto-1,3,4-thiadiazole or thiocyanuric acid (** 5) or both copolymer is used. In order to obtain an electrode for rechargeable batteries excellent in especially reversibility, it is preferred that a mole ratio of 2,5-dimercapto-1,3,4-thiadiazole and thiocyanuric acid uses a copolymer which is 1:1 to 20:1.

[0012]

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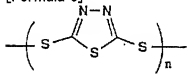
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OPERATION

[Function]The polymer of the 2,5-dimercapto-1,3,4-thiadiazole which constitutes the electrode of this invention is expressed with ** 6, and the thing of the degree of polymerization $n = 2-50$ and the molecular weights 300-7500 is used.

[0014]

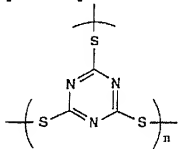
[Formula 6]



[0015]The polymer of thiocyanuric acid is expressed with ** 7, and the thing of the degree of polymerization $n = 2-50$ and the molecular weights 350-8500 is used.

[0016]

[Formula 7]



[0017]Polymers of an organic JISUFIRUDO system compound, such as these polymers and a copolymer of 2,5-dimercapto-1,3,4-thiadiazole and thiocyanuric acid, give the reversibility electrode in which high current charge and discharge are possible also at a room temperature. Without spoiling the feature of having the high energy density of a lithium cell, even if it uses as an anode for lithium cells, charge and discharge are possible and the cycle characteristic stable moreover is given. In order to obtain the anode for rechargeable batteries excellent in especially reversibility, it is preferred that the mole ratio of 2,5-dimercapto-1,3,4-thiadiazole and thiocyanuric acid uses the copolymer which is 1:1 to 20:1. A fluoro-resin, ion-conductive polymer, etc. are used as a binder. As ion-conductive polymer, the copolymer of end crosslinked polymer of the copolymer of polyethylene oxide, and ethylene oxide and propylene oxide, polyacrylonitrile, acrylonitrile, and methacrylic acid, etc. are raised. As a conducting material, conductive polymers which are carbon fiber, black lead, graphite, a metal powder, etc., such as others and poly aniline, a polythiophene, polypyrrole, and poly para-phenylene, can be used.

[0018]When using as an anode of a lithium secondary battery, the electrolysis solution which

dissolved alkali metal salt in the nonaqueous solvent is used as an electrolyte effective in an operation at a room temperature. As a nonaqueous solvent, the mixed liquor of propylene carbonate, propylene carbonate, and dimethoxyethane, The mixed liquor of propylene carbonate and a tetrahydrofuran, the mixed liquor of sulfolane and dimethoxyethane, The mixed liquor of sulfolane and a tetrahydrofuran, etc. are raised for lithium perchlorate and lithium trifluoromethanesulfonate, tetrafluoride lithium borate, lithium hexafluorophosphate, etc. as alkali metal salt again, respectively. The polymer electrolyte having contained these electrolysis solutions can also be used. As such polymer, there are end crosslinked polymer of polyethylene oxide or polypropylene oxide, end crosslinked polymer of the copolymer of ethylene oxide and propylene oxide, polyacrylonitrile, acrylonitrile, copolymerization polymer of methacrylic acid, etc. However, it is not limited to these.

[Translation done.]

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EXAMPLE

[Example]Below, the example of this invention is described in detail.

[Working example 1] 10 g of 2,5-dimercapto-1,3,4-thiadiazole (made in Tokyo Chemicals) and 5.85 g of lithium hydroxide monohydrate were dissolved in 200 ml of water, and it was considered as A liquid. Independently, the iodine 16.9g and 33.9 g of lithium iodide dihydrate were dissolved in 400 ml of water, and it was considered as B liquid. Stirring A liquid, adding B liquid was continued and oxidative polymerization was performed. After having separated the generated precipitation, and hexane, acetone, and water having washed one by one and removing an unreacted material, vacuum drying was performed at 60 °C for 10 hours. Yield is 90% and output melted into neither water nor ethanol nor ether. Since it was meltable to these solvents in the monomer, it checked that output was a polymer. 5 g and 2 g of polytetrafluoroethylene (made by poly chlorofluocarbon F-104 Daikin Industries) are mixed in the polymer powder 1g of the 2,5-dimercapto-1,3,4-thiadiazole created by the above-mentioned method, and the end (made by graphitization gaseous phase method carbon fiber Showa Denko) of carbon powder, The lump of gum paste state was created with the mortar. This lump was ground and it was considered as positive electrode mixture. Pressing of 150 mg of this mixture was carried out into the positive electrode case using the metallic mold. Tetrafluoride lithium borate was dissolved in the mixed solvent of the volume ratio 1:1 of propylene carbonate and dimethoxyethane by 1 M concentration, and it was considered as the electrolysis solution.

[0020]The coin type cell as shown in drawing 1 using an aforementioned anode, electrolysis solution, and Li metal negative electrode was constituted. As for a separator and 4, in drawing 1, an anode and 2 are [a gasket and 6] obturation boards a negative electrode and 5 a case and 3 1. When the cyclic test of charge and discharge was done for the above-mentioned cell between 3.5V and 2.65V by the constant current of 1 mA/cm², the discharge curve which has flat discharge potential was obtained, early capacity was as high as 90% of the theoretical value, and 80% of capacity of initial capacity was maintained by the 50th time. When charge and discharge were repeated between 3.5V and 2.0V, early capacity was as high as 90% of the theoretical value, and 50% of capacity of initial capacity was maintained by the 50th time.

[0021][Working example 2] 10.0 g of thiocyanuric acid (made in Tokyo Chemicals) and 7.10 g of lithium hydroxide monohydrate were dissolved in 200 ml of water, and it was considered as A liquid. Independently, the iodine 21.5g and 43.2 g of lithium iodide dihydrate were dissolved in 400 ml of water, and it was considered as B liquid. Stirring A liquid, adding B liquid was continued and oxidative polymerization was performed. After having separated the generated precipitation, and hexane, acetone, and water having washed one by one and removing an unreacted material, vacuum drying was performed at 60 °C for 10 hours. Yield is 90% and output melted into neither water nor ethanol nor ether. Since it was meltable to these solvents in the monomer, it checked that output was a polymer.

[0022]5 g and 2 g of polytetrafluoroethylene (made by poly chlorofluocarbon F-104 Daikin Industries) were mixed in the homopolymer powder 1g of the thiocyanuric acid created by the

above-mentioned method, and the end (made by graphitization gaseous phase method carbon fiber Showa Denko) of carbon powder, and the lump of gum paste state was created with the mortar. This lump was ground and it was considered as positive electrode mixture. Pressing of 150 mg of this mixture was carried out into the positive electrode case using the metallic mold, and the same coin type cell as working example 1 was constituted. When the cyclic test of charge and discharge was done for this cell between 3.5V and 2.55V by the constant current of 1 mA/cm^2 , the discharge curve which has flat discharge potential was obtained, early capacity was as high as 70% of the theoretical value, and 56% of capacity of initial capacity was maintained by the 50th time.

[0023][Working example 3] 7.5 g of 2,5-dimercapto-1,3,4-thiadiazole (made in Tokyo Chemicals), 2.5 g of thiocyanuric acid (made in Tokyo Chemicals), and 6.07 g of lithium hydroxide monohydrate were dissolved in 200 ml of water, and it was considered as A liquid. Independently, the iodine 18.4g and 36.9 g of lithium iodide dihydrate were dissolved in 400 ml of water, and it was considered as B liquid. Stirring A liquid, adding B liquid was continued and oxidative polymerization was performed. After having separated the generated precipitation, and hexane, acetone, and water having washed one by one and removing an unreacted material, vacuum drying was performed at 60 °C for 10 hours. Yield is 87% and output melted into neither water nor ethanol nor ether. Since it was meltable to these solvents in the monomer, it checked that output was a polymer. 5 g of 2,5-dimercapto-1,3,4-thiadiazole, the copolymer powder 1g of the mole ratio of 3:1 of thiocyanuric acid, and the end of carbon powder (made by graphitization gaseous phase method carbon fiber Showa Denko) and polytetrafluoroethylene (poly chlorofluorocarbon) which were created by the above-mentioned method F-104 The Daikin Industries make 2g was mixed and the lump of gum paste state was created with the mortar. This lump was ground and it was considered as positive electrode mixture. Pressing of 150 mg of this mixture was carried out into the positive electrode case using the metallic mold, and the coin type cell was constituted like working example 1.

[0024]When the cyclic test of charge and discharge was done for this cell between 3.5V and 2.55V by the constant current of 1 mA/cm^2 , the discharge curve which has flat discharge potential was obtained, early capacity was as high as 77% of the theoretical value, and 90% of capacity of initial capacity was maintained by the 50th time.

[Working example 4] 8.33 g of 2,5-dimercapto-1,3,4-thiadiazole (made in Tokyo Chemicals), 1.67 g of thiocyanuric acid (made in Tokyo Chemicals), and 6.00 g of lithium hydroxide monohydrate were dissolved in 200 ml of water, and it was considered as A liquid. Independently, the iodine 18.2g and 36.4 g of lithium iodide dihydrate were dissolved in 400 ml of water, and it was considered as B liquid. Stirring A liquid, adding B liquid was continued and oxidative polymerization was performed.

[0025]After having separated the generated precipitation, and hexane, acetone, and water having washed one by one and removing an unreacted material, vacuum drying was performed at 60 °C for 10 hours. Yield is 85% and output melted into neither water nor ethanol nor ether. Since it was meltable to these solvents in the monomer, it checked that output was a polymer. 5 g of 2,5-dimercapto-1,3,4-thiadiazole, the copolymer powder 1g of the mole ratio of 5:1 of thiocyanuric acid, and the end of carbon powder (made by graphitization gaseous phase method carbon fiber Showa Denko) and polytetrafluoroethylene (poly chlorofluorocarbon) which were created by the above-mentioned method F-104 The Daikin Industries make 2g was mixed and the lump of gum paste state was created with the mortar. This lump was ground and it was considered as positive electrode mixture. Pressing of 150 mg of this mixture was carried out into the positive electrode case using the metallic mold, and the coin type cell was constituted like working example 1. When the cyclic test of charge and discharge was done between 3.5V and 2.55V by the constant current of 1 mA/cm^2 , the discharge curve which has flat discharge potential was obtained, early capacity was as high as 87% of the theoretical value, and 98% of capacity of initial capacity was maintained by the 50th time.

[0026][Working example 5] 9.10 g of 2,5-dimercapto-1,3,4-thiadiazole (made in Tokyo Chemicals),

0.90 g of thiocyanuric acid (made in Tokyo Chemicals), and 5.72 g of lithium hydroxide monohydrate were dissolved in 200 ml of water, and it was considered as A liquid. Independently, the iodine 17.3g and 34.7 g of lithium iodide dihydrate were dissolved in 400 ml of water, and it was considered as B liquid. Stirring A liquid, adding B liquid was continued and oxidative polymerization was performed. After having separated the generated precipitation, and hexane, acetone, and water having washed one by one and removing an unreacted material, vacuum drying was performed at 60 °C for 10 hours. Yield is 80% and output melted into neither water nor ethanol nor ether. Since it was meltable to these solvents in the monomer, it checked that output was a polymer. 5 g of 2,5-dimercapto-1,3,4-thiadiazole, the copolymer powder 1g of the mole ratio of 10:1 of thiocyanuric acid, and the end of carbon powder (made by graphitization gaseous phase method carbon fiber Showa Denko) and polytetrafluoroethylene (poly chlorofluorocarbon F-104.) which were created by the above-mentioned method The Daikin Industries make 2g was mixed and the lump of gum paste state was created with the mortar. This lump was ground and it was considered as positive electrode mixture. Pressing of 150 mg of this mixture was carried out into the positive electrode case using the metallic mold, and the coin type cell was constituted like working example 1. When the cyclic test of charge and discharge was done between 3.5V and 2.55V by the constant current of 1 mA/cm², the discharge curve which has flat discharge potential was obtained, early capacity was as high as 82% of the theoretical value, and 95% of capacity of initial capacity was maintained by the 50th time. [0027][Comparative example] 5 g and 2 g of polytetrafluoroethylene (made by poly chlorofluorocarbon F-104 Daikin Industries) are mixed in the 2,5-dimercapto-1,3,4-thiadiazole (made in Tokyo Chemicals) powder 1g, and the end (made by graphitization gaseous phase method carbon fiber Showa Denko) of carbon powder, The lump of gum paste state was created with the mortar. This lump was ground and it was considered as positive electrode mixture. Pressing of 150 mg of this mixture was carried out into the positive electrode case using the metallic mold, and the coin type cell was constituted like working example 1. When the cyclic test of charge and discharge was done between 3.5V and 2.55V by the constant current of 1mA/[cm]², in the first charge and discharge, the discharge curve which has flat discharge potential was obtained, but it became 10% of capacity of initial capacity by the 10th time. The above result was summarized in Table 1 and shown. While the charge and discharge in a high current are comparatively possible for the electrode by working example, its capacity factor is also high and the cycle life is also excellent, so that clearly from Table 1.

[0028]

[Table 1]

	正極材料率 (%)	
	2サイクル目	50サイクル目
実施例1	90	72
実施例2	70	40
実施例3	77	70
実施例4	87	85
実施例5	82	78
比較例1	80	8

[0029]In working example, although metal lithium is used as a negative electrode of a rechargeable battery, the carbon compound negative electrode etc. which comprise a lithium alloy, carbon and Al powder, and solid electrolytes, such as Li-aluminum, can be used.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing of longitudinal section of the coin type cell of working example of this invention.

[Description of Notations]

- 1 Anode
- 2 Case
- 3 Separator
- 4 Negative electrode
- 5 Gasket
- 6 Obturation board

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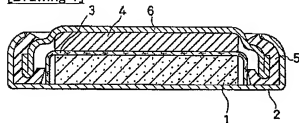
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DRAWINGS

[Drawing 1]



- 1: 正 極
3: セ バ レー タ
4: 負 極

[Translation done.]

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(54)【発明の名称】 可逆性電極

(57)【要約】

【目的】 大電流で充放電が可能な可逆性電極を提供する。

【構成】 活物質として、2, 5 - ジメルカプト 1, 3, 4 - チアジアゾールもしくはチオシアンアル酸の単体重合体または両者の共重合体など、酸化還元可能なジスルフィド系化合物の重合体を用いる。

(2)

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【特許請求の範囲】

【請求項1】 酸化還元反応が可能な有機ジスルフィド化合物の重合体と導電材および結着剤を含むことを特徴とする可逆性電池。

【請求項2】 前記有機ジスルフィド系化合物の重合体が、2, 5-ジメルカプト1, 3, 4-チアジアゾールもしくはチオシアヌル酸の単体重合体または両者の共重合体である請求項1記載の可逆性電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、二次電池、あるいはエレクトロクロミック素子などの電気化学素子に用いられる可逆性電極に関するものである。

【0002】

【従来の技術】 導電性高分子を電極材料に用いると、軽量で高エネルギー密度の電池と大面積のエレクトロクロミック素子、微小電極を用いた生物化学センサーなどの電気化学素子の実現が期待できることから、導電性高分子電極の実用が進んで検討されている。1971年に白川が発見したポリアセチレンに始まり、ポリアニリン、ポリピロール、ポリアセチレン、ポリチオフェンなどのπ電子共役系導電性高分子が見いだされ、これらを電極として用いた二次電池が開発されるに及んでいる。これらの導電性高分子を用いた電極のエネルギー密度としては、導電性高分子あたりで250～400Wh/kgであり、実際の電池を構成する段階での実効的なエネルギー密度はこの10～30%程度、すなわち20～120Wh/kgとなる。これに対し、2倍から4倍の高エネルギー密度が期待できる有機材料として、米国特許第4, 833, 048号にジスルフィド系化合物が提案されている。この化合物は、最も簡単な形でR-S-S-Rと表われ、S-S結合が電解還元によって開裂し、電解液中のカチオン(M⁺)とR-S[•]・M[•]で表わされる塩を生成する。また、この塩は、電解酸化により再び元のR-S-S-Rに戻るという性質を待つものである。また、カチオン(M⁺)を供給、錯捉する金属Mとジスルフィド系化合物を組み合わせた金属-硫黄二次電池が前述の米国特許に提案されており、電池あたり150Wh/kgと通常の二次電池に匹敵あるいはそれ以上のエネルギー密度が期待できるとされている。

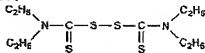
【0003】 しかしながら、提案されているジスルフィド系化合物は、米国特許第4, 833, 048号の発明者らが、ジャーナル・エレクトロケミカル・ソサイエティ、第136巻、2570～2575頁(1989)で報告しているように、元とチオラセチルチウムジスルフィド(化1)の電解では、酸化と還元電位が1V以上離れており、電極反応の教えるところによれば、このような材料における電気化学反応は、その電子移動過程が極めて遅く、従って空電付近では実用に見合う大きな電流、例えば1mA/cm²以上の電流を取り

2

出すことが困難であり、100～200℃の高温での使用に限られるという課題を有していた。

【0004】

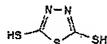
【化1】



【0005】 また、同じ発明者らが、ジャーナル・エレクトロケミカル・ソサイエティ、第139巻、2077～2081頁(1992)で報告しているところによると、2, 5-ジメルカプト1, 3, 4-チアジアゾール(化2)もしくはエタンジチオール(化3)の単体重合体または両者の共重合体や、2, 5-ジメルカプト1, 3, 4-チアジアゾールと2-メルカプトエチルエーテル(化4)の共重合体などを活物質とした電池の評価を行っている。彼らは、これらの重合体とカーボンとイオン伝導性高分子としてポリエチレンオキシドと塩を混合した電極と、ポリエチレンオキシドと塩からなる電解質と、1金属とを組み合わせて電池を構成しているが、90～110℃での作動が必要である。

【0006】

【化2】



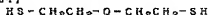
【0007】

【化3】



【0008】

【化4】



【0009】 さらに、同じ発明者らが、ジャーナル・エレクトロケミカル・ソサイエティ、第137巻、1191～1192頁(1990)で報告しているところによると、ジメチルスルホキシドに溶解したチオラセチルチウムジスルフィドを電極活物質として、正極グラファイトと負極チウムとを用いたセルにより、室温で16mA/cm²の高い電流密度で充電と放電を繰り返したことを報告している。また、3.4mA/cm²でサイクル特性を検討しているが、いずれの場合も放電深度を10%に抑えているため低容量であった。

【0010】

【発明が解決しようとする課題】 上記のように、従来提案されている有機ジスルフィド系化合物を活物質とする電池は、室温付近では大電流を取り出すことが困難であり、容量が低いなど実用性に乏しいものであった。本発明は、このような問題を解決し、室温でも大電流での充放電が可能な可逆性電極を提供することを目的とする。

(3)

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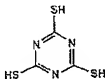
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[0011]

【課題を解決するための手段】本発明の可逆性電極は、有機ジスルフィド系化合物の重合体を活性物質とし、さらに結着剤と導電材を含んでいる。また、有機ジスルフィド系化合物の重合体としては、2,5-ジメルカプト1,3,4-チアジアゾールもしくはチオシアヌル酸（化5）の単量重合体または両者の共重合体を用いる。特に可逆性に優れた二次電池用電極を得るためには、2,5-ジメルカプト1,3,4-チアジアゾールとチオシアヌル酸のモル比が1:1から20:1である共重合体を用いることが好ましい。

[0012]

[化5]

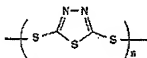


[0013]

【作用】本発明の電極を構成する2,5-ジメルカプト1,3,4-チアジアゾールの重合体は化6で表わされ、重合度 $n=2\sim50$ 、分子量300~7500のものを用いられる。

[0014]

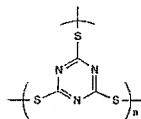
[化6]



[0015] また、チオシアヌル酸の重合体は化7で表わされ、重合度 $n=2\sim50$ 、分子量350~8500のものを用いられる。

[0016]

[化7]



[0017] これらの重合体、および2,5-ジメルカプト1,3,4-チアジアゾールとチオシアヌル酸との共重合体など、有機ジスルフィド系化合物の重合体は、室温でも大電流充放電が可能な可逆性電極を与える。また、リチウム電池用正極として用いても、リチウム電池の高エネルギー密度を有するという特徴を損なわずに充

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放電が可能で、しかも安定したサイクル特性を与える。特に可逆性に優れた二次電池用正極を得るためには、2,5-ジメルカプト1,3,4-チアジアゾールとチオシアヌル酸のモル比が1:1から20:1である共重合体を用いることが好ましい。また、結着剤としては、フッ素樹脂やイオン伝導性ポリマーなどが用いられる。イオン伝導性ポリマーとしては、ポリエチレンオキシドや、エチレンオキシドとプロピレンオキシドの共重合体の未架橋ポリマー、ポリアクリロニトリルやアクリロニトリルとメタクリル酸の共重合体などがあげられる。導電材としては、炭素繊維、黒鉛、グラファイト、金属粉などの他、ポリビニール、ポリアニリン、ポリチオフェン、ポリパラフェニレンなどの導電性ポリマーを用いることができる。

[0018] また、リチウム二次電池の正極として用いる場合、室温での作動に有効な電解質として、アルカリ金属塩を非水溶媒に溶解した電解液が用いられる。非水溶媒としては、プロピレンカーボネート、プロピレンカーボネートとジメチルエタンの混合液、プロピレンカーボネートとテトラヒドロフランの混合液、スルホランとジメチルエタンの混合液、スルホランとテトラヒドロフランの混合液などが、またアルカリ金属塩としては、過塩素酸リチウム、トリフルオロメタンスルホン酸リチウム、四フッ化ホウ酸リチウム、六フッ化リン酸リチウムなどがそれぞれあげられる。さらに、これらの電解液を含んだポリマー電解質も用いることができる。このようなポリマーとしては、ポリエチレンオキシドやポリプロピレンオキシドの未架橋ポリマー、エチレンオキシドとプロピレンオキシドの共重合体の未架橋ポリマー、ポリアクリロニトリルやアクリロニトリルとメタクリル酸の共重合ポリマーなどがある。しかし、これらに限定されるものではない。

[0019]

【実施例】以下に、本発明の具体例について詳細に述べる。

【実施例1】2,5-ジメルカプト1,3,4-チアジアゾール（東京化成製）10gと水酸化リチウム・水合物5,85gを水200mlに溶解し、A液とした。別に、ヨウ素16,9gとヨウ化リチウム・水合物3,9gを水400mlに溶解し、B液とした。A液を保持しながら、B液を添加し続け、酸化重合を行なった。生成した沈澱を分離し、ヘキサン、アセトン、水で順次洗浄して、未反応物を除去した後、60℃で10時間、真空乾燥を行なった。収率は90%で、生成物は水、エタノール、エーテルのいずれにも溶けなかった。単量体でこれらの溶媒に可溶であることから生成物が重合体であることを確認した。上記の方法で作成した2,5-ジメルカプト1,3,4-チアジアゾールの重合体粉末1gと炭素粉末（黒鉛化気相法炭素繊維 昭和電気工）5gとポリテトラフルオロエチレン（ポリフロン F-10

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4. ダイキン工業製) 2gを混合し、乳鉢でガムベース状の固まりを作成した。この固まりを粉砕し、正極合剤とした。この合剤150mgを金型を用いて正極ケース内に加圧成形した。ポリレンカーボネートとジメチルシロキサン(体積比1:1)の混合溶媒に1M濃度で四つ化ボリチウムを溶解し、画液調製した。

【0020】前記の正極と電解液およびLi⁺金属負極を用いて図1に示すようなコイン型電池を構成した。図1において、1は正極、2はケース、3はセパレータ、4は負極、5はガasket、6は封口部である。上記の電池を1mA/cm²の定電流で3.5Vと2.65Vの間で充電・放電の繰り返し試験を行なったところ、平坦な放電電位を有する放電カーブが得られ、初期の容量が理論値の90%と高く、50回目まで初期容量の80%の容量が維持されていた。さらに、3.5Vと2.0Vの間で充電と放電を繰り返し続けたところ、初期の容量が理論値の90%と高く、50回目まで初期容量の50%の容量が維持されていた。

【0021】【実施例2】チオシアヌル酸(東京化成製)10.0gと水酸化リチウム水和物7.10gを水200mlに溶解し、A液とした。別に、ヨウ素21.5gとヨウ化リチウム二水和物4.3.2gを水400mlに溶解し、B液とした。A液を攪拌しながら、B液を添加し続け、酸化重合を行なった。生成した沈殿を分離し、ヘキサ、アセトン、水で順次洗浄して、未反応物を除去した後、60℃で10時間、真空乾燥を行なった。収率は90%で、生成物は水、エタノール、エーテルのいずれにも溶けなかった。単量体がこれらの溶媒に可溶であることから生成物が重合体であることを確認した。

【0022】上記の方法で作成したチオシアヌル酸の単量体粉末1gと炭素粉末(黒鉛化炭素相炭素繊維 昭和電工製)5gとポリテトラフルオロエチレン(ポリフロン F-104 ダイキン工業製)2gを混合し、乳鉢でガムベース状の固まりを作成した。この固まりを粉砕し、正極合剤とした。この合剤150mgを金型を用いて正極ケース内に加圧成形し、実施例1と同様のコイン型電池を構成した。この電池を1mA/cm²の定電流で3.5Vと2.65Vの間で充電・放電の繰り返し試験を行なったところ、平坦な放電電位を有する放電カーブが得られ、初期の容量が理論値の70%と高く、50回目まで初期容量の56%の容量が維持されていた。

【0023】【実施例3】2.5-ジメチルカプト1, 3, 4-チアジアゾール(東京化成製)7.5gとチオシアヌル酸(東京化成製)2.5gと水酸化リチウム水和物6.07gを水200mlに溶解し、A液とした。別に、ヨウ素18.4gとヨウ化リチウム二水和物36.9gを水400mlに溶解し、B液とした。A液を攪拌しながら、B液を添加し続け、酸化重合を行な

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た。生成した沈殿を分離し、ヘキサ、アセトン、水で順次洗浄して、未反応物を除去した後、60℃で10時間、真空乾燥を行なった。収率は87%で、生成物は水、エタノール、エーテルのいずれにも溶けなかった。単量体がこれらの溶媒に可溶であることから生成物が重合体であることを確認した。上記の方法で作成した2.5-ジメチルカプト1, 3, 4-チアジアゾールとチオシアヌル酸の3:1のモル比の共重合体粉末1gと炭素粉末(黒鉛化炭素相炭素繊維 昭和電工製)5gとポリテトラフルオロエチレン(ポリフロン F-104 ダイキン工業製)2gを混合し、乳鉢でガムベース状の固まりを作成した。この固まりを粉砕し、正極合剤とした。この合剤150mgを金型を用いて正極ケース内に加圧成形し、実施例1と同様にしてコイン型電池を構成した。

【0024】この電池を1mA/cm²の定電流で3.5Vと2.65Vの間で充電・放電の繰り返し試験を行なったところ、平坦な放電電位を有する放電カーブが得られ、初期の容量が理論値の77%と高く、50回目まで初期容量の90%の容量が維持されていた。

【実施例4】2.5-ジメチルカプト1, 3, 4-チアジアゾール(東京化成製)8.33gとチオシアヌル酸(東京化成製)1.67gと水酸化リチウム水和物6.00gを水200mlに溶解し、A液とした。別に、ヨウ素18.2gとヨウ化リチウム二水和物36.4gを水400mlに溶解し、B液とした。A液を攪拌しながら、B液を添加し続け、酸化重合を行なった。

【0025】生成した沈殿を分離し、ヘキサ、アセトン、水で順次洗浄して、未反応物を除去した後、60℃で10時間、真空乾燥を行なった。収率は85%で、生成物は水、エタノール、エーテルのいずれにも溶けなかった。単量体がこれらの溶媒に可溶であることから生成物が重合体であることを確認した。上記の方法で作成した2.5-ジメチルカプト1, 3, 4-チアジアゾールとチオシアヌル酸の5:1のモル比の共重合体粉末1gと炭素粉末(黒鉛化炭素相炭素繊維 昭和電工製)5gとポリテトラフルオロエチレン(ポリフロン F-104 ダイキン工業製)2gを混合し、乳鉢でガムベース状の固まりを作成した。この固まりを粉砕し、正極合剤とした。この合剤150mgを金型を用いて正極ケース内に加圧成形し、実施例1と同様にしてコイン型電池を構成した。1mA/cm²の定電流で3.5Vと2.65Vの間で充電・放電の繰り返し試験を行なったところ、平坦な放電電位を有する放電カーブが得られ、初期の容量が理論値の87%と高く、50回目まで初期容量の98%の容量が維持されていた。

【0026】【実施例5】2.5-ジメチルカプト1, 3, 4-チアジアゾール(東京化成製)9.10gとチオシアヌル酸(東京化成製)0.90gと水酸化リチウム水和物5.72gを水200mlに溶解し、A液と

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した。別に、ヨウ素17.3gとヨウ化リチウム二水和物34.7gを水400mlに溶解し、B液とした。A液を攪拌しながら、B液を追加し続け、酸化重合を行なった。生成した試料を分離し、ヘキサン、アセトン、水で順次洗浄して、未反応物を除去した後、60℃で10時間、真空乾燥を行なった。収率は80%で、生成物は水、エタノール、エーテルのいずれにも溶けなかった。単量体がこれらの溶媒に可溶であることから生成物が重合体であることを確認した。上記の方法で作成した2、5-ジメルカプト1,3,4-チアジアゾールと炭素粉末（黒鉛化炭相法炭素繊維 昭和電工製）5gとポリテトラフルオロエチレン（ポリフロン F-104 ダイキン工業製）2gを混合し、乳鉢でガムペースト状の固まりを作成した。この固まりを粉砕し、正極合剤とした。この合剤150mgを金型を用いて正極ケース内に加压成形し、実施例1と同様にコイン型電池を構成した。1mA/cm²の定電流で3.5Vと2.55Vの間で充電・放電の繰り返し試験を行なったところ、平坦な放電電位を有する放電カーブが得られ、初期の容量が理論値の82%と高く、50回目で初期容量の95%の容量が維持されていた。

【0027】【比較例】2、5-ジメルカプト1,3,4-チアジアゾール（東京化成製）粉末1gと炭素粉末（黒鉛化炭相法炭素繊維 昭和電工製）5gとポリテトラフルオロエチレン（ポリフロン F-104 ダイキン工業製）2gを混合し、乳鉢でガムペースト状の固まりを作成した。この固まりを粉砕し、正極合剤とした。この合剤150mgを金型を用いて正極ケース内に加压成形し、実施例1と同様にコイン型電池を構成した。1mA/cm²の定電流で3.5Vと2.55Vの間で充電・放電の繰り返し試験を行なったところ、一回目の充電で平坦な放電電位を有する放電カーブが得られたが、10回目で初期容量の10%の容量となった。*

*た、以上の結果を表1にまとめて示した。表1から明らかなように、実施例による電極は、比較的大電流での充放電が可能であるとともに、利用率が高く、かつサイクル寿命も優れている。

【0028】

【表1】

	正極材料 %	
	2サイクル目	50サイクル目
実施例1	90	72
実施例2	70	40
実施例3	77	70
実施例4	87	85
実施例5	82	78
比較例1	80	8

【0029】実施例では、二次電池の負極として金属リチウムを用いているが、この他にLi-A1などのリチウム合金や、カーボンとA1粉末と固体電解質で構成されるカーボン複合負極などを用いることができる。

【0030】

【発明の効果】本発明によれば、比較的大電流での充放電が可能な可逆性電極を得ることができる。

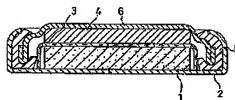
【図面の簡単な説明】

【図1】本発明の実施例のコイン型電池の縦断面図である。

【符号の説明】

- 1 正極
- 2 ケース
- 3 セパレータ
- 4 負極
- 5 ガスケット
- 6 封口板

【図1】



- 1: 正極
3: セパレータ
4: 負極